PARA-ALKYLATION OF BENZOYLDURENE BY THE GRIGNARD REAGENT

BY

BLAINE CHASE McKUSICK

B. Ch. E., University of Minnesota, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE SCHOOL OF THE UNIVERSITY
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Introduction

Among the many known examples of the addition of Grignard reagents and conjugated systems are a few which are peculiar in that the conjugated system in question involves an aromatic nucleus. Conjugate addition of aryl Grignard reagents to certain mesityl aryl ketones, for example, has been found to arylate the ketone in an ortho position of the unhindered aryl radical[1,2]. In these reactions it appeared that 1,4-addition had occurred.

Steric inhibition of normal or 1,2-addition by the mesityl radical offered an explanation of the abnormal attack of the Grignard reagent. This idea suggested that similar results might be obtained with other aryl ketones possessing excessive crowding about the carbonyl group. In the present work an attempt was made to test this hypothesis by subjecting duryl phenyl ketone to the action of Grignard reagents.

Discussion

Benzoyldurene, prepared by the action of benzoyl chloride on durene in the presence of aluminum chloride, was treated with benzylmagnesium chloride. A reaction proceeded under mild conditions to give a diaryl ketone in twenty per cent yield. That the product was not the expected ortho alkylated product, 2′-benzyl-2,3,5,6-tetramethylbenzophenone, was proved by comparison with the authentic sample obtained by condensing duroyl chloride with the Grignard reagent from 2-bromodiphenylmethane.

It seemed likely that the benzoyl group had entered a para position. The para position in the durene ring is known to be the most reactive to bromination and acylation of any position in benzoyldurene. Hence 4-benzyl-2,3,5,6-tetramethylbenzophenone was synthesized as the more probable para alkylation product. Sodium and alcohol reduced benzoyldurene to benzyl-

durene, and condensation of the latter with benzoyl chloride gave 4-benzyl-2,3,5,6-tetramethylbenzophenone, but its properties did not agree with those of the benzoyldurene-benzylmagnesium chloride reaction product.

4′-Benzyl-2,3,5,6-tetramethylbenzophenone proved to be the correct structure. It was successfully synthesized by condensing *p*-benzylbenzoyl chloride with durene by the Friedel-Crafts method. Its structure was confirmed by cleaving the ketone to durene and *p*-benzylbenzoic acid with hot, syrupy phosphoric acid.

Benzoyldurene was found to react with *t*-butylmagnesium chloride in similar fashion to yield 4′-*t*-butyl-2,3,5,6-tetramethylbenzophenone. It was synthesized from duroyl chloride and bis(*p*-*t*-butylphenyl)cadium. Cleavage with phosphoric acid gave durene and *p*-*t*-butylbenzoic acid. Nitration resulted in a dinitro derivative. Bromination yielded a monobromide, 4′-*t*-butyl-2,3,5,6-tetramethyl-4-bromobenzophenone. The latter could be prepared in forty per cent yield by addition of *t*-butylmagnesium chloride to 4-bromo-2,3,5,6-tetramethylbenzophenone, obtained either by bromination of benzoyldurene or a Friedel-Crafts reaction between bromodurene and benzoyl chloride.

It was found that many of the dairyl ketones could be reduced by sodium and alcohol[3] to the corresponding diarylmethane. The diarylmethanes were useful solid derivatives.

It is highly probable that para alkylation of zenzoyldurene by the Grignard reagent occurs by 1,6 addition. This implies the formation of an intermediate dihydroaromatic structure which readily loses one molecule of hydrogen to give a fully aromatic compound. The mechanism by which this oxidation or dehydrogenation takes place is as yet unknown.

But five cases of 1,6-addition of the Grignard reagent to a conjugated system are to be found in the literature[4]. All involve ketones related to fuchsone. In the present instance, the occurrence of 1,6-addition rather than 1-4-addition can be ascribed to steric hindrance. Stuart models indicate that methyl groups in the duryl ring provide enough hindrance around the ortho positions of the phenyl ring to prevent any but small radicals like

methyl, or planar radicals like phenyl, from adding there. The relative electronegativity[5] of the Grignard reagent radical may be a contributing factor.

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Vita

The author was born in Minneapolis on March 22, 1918. After attending the public schools of that city, he entered the University of Minnesota, and graduated in chemical engineering in 1940. He entered the University of Illinois as a teaching assistant in organic chemistry in the fall of 1940. He held a Rohm and Haas Research Assistantship during 1942-1943 and was a Special Research Assistant in 1943-1944.

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